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(54) Title: HYDROCARBON GAS MIXTURE FOR THE UNDER-PRESSURE CARBURIZING OF STEEL

(57) Abstract: The subject of present invention relates to mixture for carburizing of steel products, mainly parts of machines, vehicles and every mechanical apparatus, used in vacuum furnaces. Present invention relates to mixture for under-pressure carburizing containing the carbon carrier comprising two unsaturated hydrocarbons, likely ethylene and acetylene, in volume ratio from 0.1 to 2.00. The carbon carrier can be further mixed with hydrogen or ammonia.

# HYDROCARBON GAS MIXTURE FOR THE UNDER-PRESSURE CARBURIZING OF STEEL

The object of the present invention relates to a mixture used in vacuum furnaces for under-pressure carburizing of steel products, mainly parts of machines, vehicles and all sorts of mechanical apparatuses.

From the US Patent 5,702,540 a process is known, in which a charge is processed under vacuum in the presence of a carbon carrier which contains unsaturated aliphatic hydrocarbons, where the pressure in the chamber shall not be higher than 1 kPa.

Another US Patent, 6,187,111, uses gaseous ethylene as the carbon carrier and the pressure in the chamber shall be within the range of 1 to 10 kPa, whereas the charge shall have the temperature between 900°C and 1100°C.

The patent EPO 0,882,811 is also known in which the carbon carrier is a hydrocarbon with a strict 1:1 carbon-to-hydrogen ratio.

To obtain the required carburizing result the carbon carrier, ethylene or acetylene, is introduced to a hot vacuum furnace chamber during the carburizing stage either in a continuous or a pulse manner. The carbon carrier can be introduced together with other chemically inert gases, e.g. nitrogen, argon, or active gases, e.g. hydrogen, in order to control the efficiency and cleanness of the carburizing process, as well as with active nitrogen carriers, e.g. ammonia, for carbonitriding of steel.

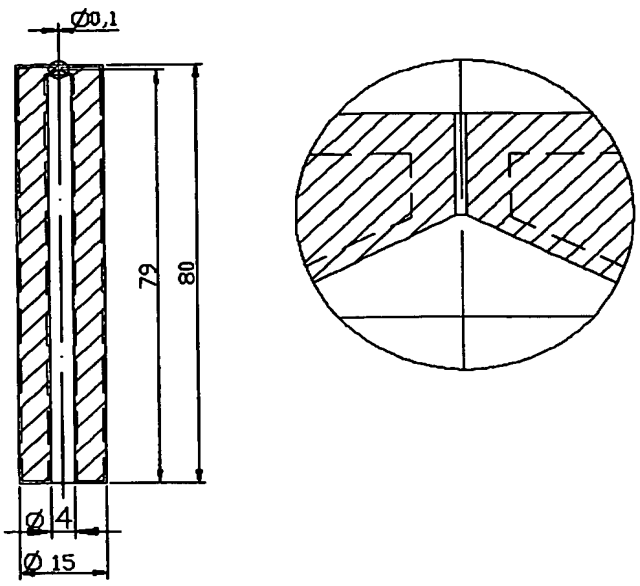
The main point and essence of the present invention is the mixture for under-pressure carburizing , which contains the carbon carrier in the form of two unsaturated hydrocarbons, having the volume ratio from 0.1 to 2.00, preferably from 0.15 to 2.0. The carbon carrier is preferably ethylene and acetylene. The carbon carrier can be further mixed with hydrogen or also with ammonia. In the case of mixing the carbon carrier with hydrogen, 0,7 to 1 volume by ratio should be maintained. For ammonia this ratio is 0.7 to 5.0.

The mixture according to the present invention is characterized by the effect of synergy of uniform carburizing of intricate shape workpieces, especially those with narrow and deep hollows of complicated shapes and recesses, and effective elimination of side-products of vacuum carburizing of steels such as soot and tar.

One of possible implementations of the mixture for under-pressure carburizing according to the present invention is illustrated by the following examples, while the surfaces of the samples are shown in the figure enclosed.

**Example 1**

A furnace chamber of the size 200x200x400 mm was charged with workpieces made of low carbon steel grades together with three samples made of 16CrMn5 with deep, narrow hollows of intricate shapes. The total surface area of the charge was 0.4 $m^2$. After heating under vacuum up to 950°C the carbon carrier was introduced - comprising ethylene and acetylene in the volume ratio 1, mixed with hydrogen in the volume ratio 1,17 - with constant flow rate 190 l/hr and pressure pulse was generated in the furnace chamber within the range of 3 to 8 mbar. Steel workpieces were heated 20 minutes under this atmosphere at the temperature of 950°C, then under vacuum for 10 minutes and they were then cooled down to the ambient temperature. On the surface of all the samples including the entire cross section of the deep hollow of intricate shape, the carburizing layer was formed. The layer was of a uniform perlitic structure without precipitation of secondary carbides and of a uniform depth of 0.44 ± 0.05 mm measured according to the limit structure of 50% perlite and 50% ferrite. No evidence of soot and tar was found either on the surface of workpieces after carburizing or in the furnace chamber interior.




**Example 2**

A furnace chamber of the size 200x200x400 mm was charged with workpieces made of low carbon steel grades together with three samples with made of 17CrNi with deep, narrow hollows of intricate shapes. The total surface area of the charge was 0.4 $m^2$. After heating under vacuum up to 950°C the carbon carrier was introduced - comprising ethylene and acetylene in the volume ratio 1.83, mixed with hydrogen in the volume ratio 1,45 - with constant flow rate 208 l/hr and pressure pulse was generated in the furnace chamber within the range of 3 to 8 mbar. Steel workpieces were heated 20 minutes under this atmosphere at the temperature of 950°C, then under vacuum for 30 minutes, and then fast cooled to the ambient temperature under 6 bar nitrogen pressure. On the surface of all the samples including the entire cross section of the deep hollow of intricate shape, the carburizing layer was formed. The layer was of a uniform martenzitic structure without precipitation of secondary carbides and of a uniform depth of 0.46 ± 0.05 mm measured according to the minimum limit hardness of 500 $HV_{01}$. No evidence of soot and tar was found either on the surface of workpieces after carburizing or in the furnace chamber interior.

## CLAIMS:

1. The mixture for under-pressure carburizing employing hydrocarbons **is characterized in that** it contains the carbon carrier in the form of two unsaturated hydrocarbons in the proportion from 0.1 to 2.0, where the said carbon carrier can be further mixed with other components modifying the carburizing process.
2. The mixture for under-pressure carburizing according to claim 1 **is characterized in that** it is beneficial and preferable to have the said hydrocarbons in the proportion of from 0.15 to 2.0.
3. The mixture for under-pressure carburizing according to claim 1 **is characterized in that** it is most beneficial and preferable if the said carbon carrier is a mixture of ethylene and acetylene.

   the said carbon carrier should preferably be a mixture of ethylene and acetylene
4. The mixture for under-pressure carburizing according to claim 1 **is characterized in that** the said carbon carrier can be mixed with hydrogen in the proportion from 0.7 to 1.6.
5. The mixture for under-pressure carburizing according to claim 1 **is characterized in that** the said carbon carrier can be mixed with ammonia in the proportion from 0.7 to 5.0.

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PCT/[redacted] 03/00066

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C8/22 C21D1/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C C21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, METADEX, PAJ, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 2000, no. 04;<br>31 August 2000 (2000-08-31)<br>& JP 2000 001765 A (NACHI FUJIKOSHI CORP),<br>7 January 2000 (2000-01-07) | 1-3 |
| Y | paragraph 24 of patent document<br>abstract | 4,5 |
| Y | EP 0 818 555 A (JH CORP)<br>14 January 1998 (1998-01-14)<br>column 4, line 3-13,45-50 | 4,5 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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| Name and mailing address of the ISA | Authorized officer |
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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Badcock, G |

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Inter[redacted] Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | KULA, P. (TECHNICAL UNIVERSITY OF LODZ) ET AL: "New vacuum carburizing technology." HEAT TREATING PROGRESS (FEB.-MAR. 2001) 1, (1), 57-60, GRAPHS, PHOTOMICROGRAPHS, 6 REF., XP009023937 page 58-59 | 4,5 |
| A | SUGIYAMA M ET AL: "VACUUM CARBURIZING WITH ACETYLENE" ADVANCED MATERIALS & PROCESSES, AMERICA SOCIETY FOR METALS. METALS PARK, OHIO, US, vol. 155, no. 4, April 1999 (1999-04), pages H29-H33, XP000866805 ISSN: 0882-7958 page 2 -page 3 | 1-5 |
| A | PATENT ABSTRACTS OF JAPAN vol. 2002, no. 11, 6 November 2002 (2002-11-06) & JP 2002 194526 A (DOWA MINING CO LTD), 10 July 2002 (2002-07-10) abstract | 1-5 |

# INTERNATIONAL SEARCH REPORT

[redacted] on patent family members

Inter[redacted]al Application No
PCT/[redacted]03/00066

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| JP 2000001765 A | 07-01-2000 | NONE | |
| EP 0818555 A | 14-01-1998 | AT 203063 T | 15-07-2001 |
| | | CA 2215897 A1 | 03-10-1996 |
| | | DE 69613822 D1 | 16-08-2001 |
| | | DE 69613822 T2 | 04-04-2002 |
| | | EP 0818555 A1 | 14-01-1998 |
| | | CN 1184510 A | 10-06-1998 |
| | | JP 2963869 B2 | 18-10-1999 |
| | | JP 8325701 A | 10-12-1996 |
| | | WO 9630556 A1 | 03-10-1996 |
| — | — | TW 400394 B | 01-08-2000 |
| | | US 5702540 A | 30-12-1997 |
| JP 2002194526 A | 10-07-2002 | NONE | |